



Behaviour of Nafion[®] 350 membrane in sodium sulfate electrochemical splitting: continuous process modelling and pilot scale tests

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Abstract

A two-compartment membrane electrolysis cell is used to split sodium sulfate into sulfuric acid and sodium hydroxide. The cell is equipped with a Nafion[®] 350 cation-exchange membrane. Due to the dissociation of the strong acid, free hydrogen ions migrate through the membrane together with sodium ions. This transfer decreases current efficiency. The transport properties of Nafion[®] 350 membrane are studied in a laboratory cell. Current efficiency varies either with sulfuric acid to total sulfate concentration ratio in the anolyte or with sodium hydroxide concentration depending on the membrane state. Water transport through the membrane is due to electroosmosis. Hydrogen and sodium ions carry three to four molecules of water per ion. Modelling of a continuous feed and bleed process in the steady-state is performed using material balance and transport data obtained in a laboratory scale. Tests in a pilot plant (scaling factor 13) were undertaken. The model predictions agree well with experimental results. As a consequence, the model may be used for industrial purposes. Due to current efficiency decrease when salt conversion increases, the use of a cascade of cells in series is advantageous compared to a single stage.

List of symbols

| | |
|-----------------------------|---|
| [A] | Concentration of the species A (mol dm ⁻³) |
| C _H | total acidic hydrogen concentration: $C_H = [\text{HSO}_4^-] + [\text{H}^+]$ (mol dm ⁻³) |
| C _{SO₄} | total sulfate concentration: $C_{\text{SO}_4} = [\text{HSO}_4^-] + [\text{SO}_4^{2-}]$ (mol dm ⁻³) |
| F | Faraday constant (26.8 A h mol ⁻¹ or 96485 A s mol ⁻¹) |
| J | current density (A m ⁻²) |
| M | molar mass (kg kmol ⁻¹) |
| m | water mass flowrate (kg h ⁻¹) |
| n | number of moles (kmol) |
| Q | volumetric flowrate (dm ³ h ⁻¹) |
| s | membrane and electrode active surface (m ²) |
| t | transport number |
| V | volume (dm ³) |

| | |
|---|--|
| W | specific water transport rate (kg m ⁻² h ⁻¹) |
| X | sulfuric acid to total sulfate concentration ratio in the anolyte ($X = C_H/2C_{\text{SO}_4}$) |

Greek letters

| | |
|---|---|
| α | anolyte volume variation per mole of charge passed in the cell (dm ³ faraday ⁻¹) |
| θ | time (h) |
| ρ | density (kg dm ⁻³) |

Subscripts

| | |
|-----|---|
| a | anolyte |
| c | catholyte |
| in | inlet |
| m | membrane |
| out | outlet |
| th | theoretical (which correspond to 100% current efficiency) |

1. Introduction

Membrane electrolysis is a process that associates selective ion transport through an ion-exchange membrane and electrochemical reactions at the electrodes. It is widely used for chlor-alkali production and has many other applications, in organic synthesis or fuel cells for

example [1]. Acid and alkali regeneration from spent sodium sulfate solutions has been studied [2–4]. Notably, Jörissen et al. [2] used a Nafion[®] 390 membrane and showed that sodium transport is either a function of acid to salt ratio in the anolyte or a function of sodium hydroxide concentration in the catholyte depending on the relative concentrations values. Water transport was

not considered in this study. Otherwise, to our knowledge, there has been no published literature on the modelling of a continuous sodium sulfate electrolysis process, and no scaling-up experiments. In the chlor-alkali application, Chandran et al. [5] studied the mass and energy balance of a continuous process using a laboratory cell (area 34.3 cm²). Sodium and water transport data used for computation were taken from published papers. Experimental verification of the model was undertaken in the laboratory scale. However, the authors did not experimentally show that the model is still accurate in a larger scale.

Sodium sulfate splits into sulfuric acid and sodium hydroxide in a two-compartment cell such as shown schematically in Figure 1. The anode reaction generates hydrogen ion and oxygen from water oxidation (i.e., $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$) and the cathode reaction generates hydroxyl ion and hydrogen from water reduction (i.e., $4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- + 2\text{H}_2$). Due to the electric field, sodium ions migrate through the cation-exchange membrane from the anolyte to catholyte.

In this configuration, hydrogen ions in the anolyte also migrate through the membrane and react with hydroxyl ions near the interface membrane–catholyte if the membrane is perfectly permselective to cations. However, seeing that the membrane is not perfectly impermeable to hydroxyl ions two situations must be considered [2]: (a) When acid concentration is high and sodium hydroxide concentration is low, hydrogen ions cross the cation-exchange membrane from the anode compartment to the cathode compartment where they neutralise hydroxyl ions. The membrane is in ‘acidic state’ (i.e., proton crosses the membrane). (b) In contrast, when acid concentration is low and sodium hydroxide concentration is high, hydroxyl ions cross the membrane from cathode compartment to anode compartment, neutralising acid. The membrane is in

‘alkaline state’ (i.e., hydroxyl ion crosses the membrane).

Other species that could be transferred through the membrane are as follows: (i) sulfate and hydrogenosulfate ions, but this transfer (by diffusion) will be against the electric field and is practically negligible as checked experimentally, and (ii) water, as it is known that cations transport water molecules either as water of hydration or as water pumped hydrodynamically [6].

The present paper report is twofold. First, the evaluation of mass transport through Nafion[®] 350 membrane during sodium sulfate electrochemical splitting into sulfuric acid and sodium hydroxide such as is shown in Figure 1. A two-compartment laboratory cell, the area of which is 32 cm², is used (electrodes and membrane areas are equal). Acid and salt mixtures are fed to the anode compartment and sodium hydroxide solution to the cathode compartment. The transport numbers of sodium and hydrogen or hydroxyl ions are determined. Water transport number is also determined. Secondly, the modelling and scaling-up of a steady-state feed and bleed electrolysis operation. The model is based on the mass balance equations for the anolyte and the catholyte and uses the laboratory results concerning ion transport numbers and water transport through the membrane. Tests in pilot scale (scaling up factor 13) are reported.

Nafion[®] 350 membrane (a perfluorosulfonic membrane), used in this study, is composite of two equivalent weights of polymer. The side facing the cathode has a higher exchange capacity than the other side allowing more efficient exclusion of hydroxyl ions [7]. Liao et al. [8] used this membrane and showed an enhanced rejection of chloride ions compared to Nafion[®] 117 membrane. This membrane with strong acid exchange groups is recommended when using an acid electrolyte.

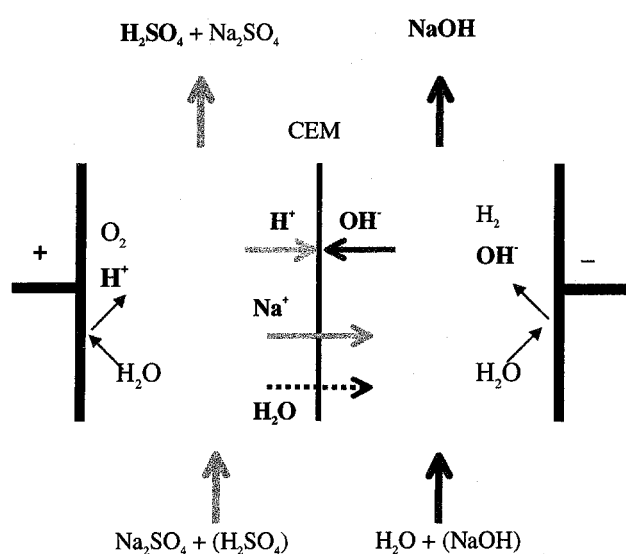


Fig. 1. Sodium sulfate electrochemical splitting in a two-compartment cell (hydrogen and hydroxyl ions migration cannot exist together).

2. Mass balance in steady-state feed and bleed process

The following relations respectively describe ion transport in the ‘acidic or alkaline state’ of the membrane:

$$t_{m,\text{Na}^+} + t_{m,\text{H}^+} = 1 \quad (1)$$

$$t_{m,\text{Na}^+} + t_{m,\text{OH}^-} = 1 \quad (2)$$

These relations mean that current is transported in the membrane by Na⁺ and H⁺ or by Na⁺ and OH⁻. Assuming that there is no current loss via the inlet and outlet pipes, the current efficiency is simply equal to the sodium ion transport number.

The studied feed and bleed process is shown in Figure 2. It is assumed that the steady-state is reached, that the anolyte and the catholyte flows are perfectly stirred and that the loss of water by evaporation is negligible. Mass balance is carried out by considering that the membrane is in the ‘acidic state’ since this state

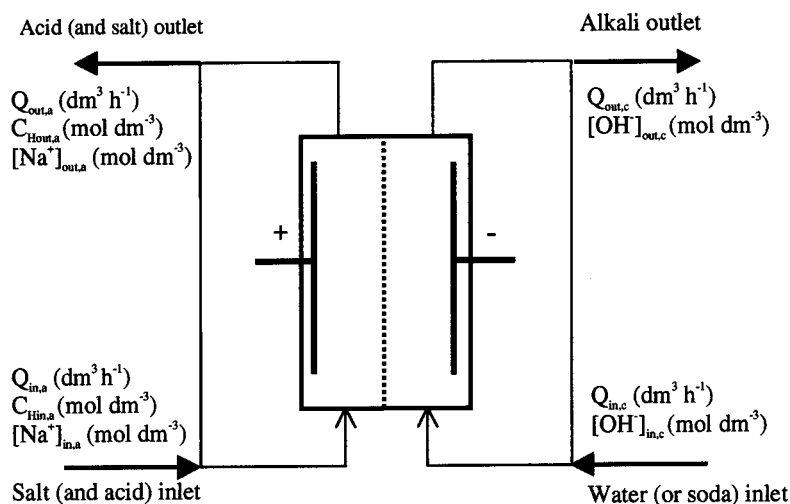


Fig. 2. Feed and bleed operation.

means large salt conversion (in the 'alkaline state' minor modifications must be carried out).

Total acidic hydrogen in the anolyte:

$$C_{\text{Hin},a}Q_{\text{in},a} + \frac{Js}{F} = \frac{t_{\text{m},\text{H}^+}Js}{F} + C_{\text{Hout},a}Q_{\text{out},a} \quad (3)$$

Sodium ion in the anolyte:

$$[\text{Na}^+]_{\text{in},a}Q_{\text{in},a} = \frac{t_{\text{m},\text{Na}^+}Js}{F} + [\text{Na}^+]_{\text{out},a}Q_{\text{out},a} \quad (4)$$

Total anolyte mass balance:

$$\begin{aligned} \rho_{\text{in},a}Q_{\text{in},a} &= \rho_{\text{out},a}Q_{\text{out},a} + \frac{Js}{4F}M_{\text{O}_2} + m_{\text{m}} \\ &+ \frac{t_{\text{m},\text{Na}^+}Js}{F}M_{\text{Na}} + \frac{t_{\text{m},\text{H}^+}Js}{F}M_{\text{H}} \end{aligned} \quad (5)$$

Sodium hydroxide in the catholyte:

$$[\text{OH}^-]_{\text{in},c}Q_{\text{in},c} + \frac{Js}{F} - \frac{t_{\text{m},\text{H}^+}Js}{F} = [\text{OH}^-]_{\text{out},c}Q_{\text{out},c} \quad (6)$$

Total catholyte mass balance:

$$\begin{aligned} \rho_{\text{in},c}Q_{\text{in},c} + m_{\text{m}} + \frac{t_{\text{m},\text{Na}^+}Js}{F}M_{\text{Na}} + \frac{t_{\text{m},\text{H}^+}Js}{F}M_{\text{H}} \\ = \rho_{\text{out},c}Q_{\text{out},c} + \frac{Js}{2F}M_{\text{H}_2} \end{aligned} \quad (7)$$

The different terms in these equations refer to: inlet flow, outlet flow, ions transport through the membrane (sodium and hydrogen ions), water mass flow-rate through the membrane (m_{m}), production of oxygen gas and H^+ at the anode (respectively, 4 and 1 faraday per mole), and production of hydrogen gas and OH^- at the cathode (respectively 2 and 1 faraday per mole).

To solve these equations the variation of ion transport numbers and water transport through the membrane should be known. Densities are also required.

3. Experimental details

All the chemicals used in the laboratory studies were analytical grade. The sodium sulfate used in pilot experiments was a pure grade product. Acid and alkali concentrations were determined by titration method using NaOH or HCl solutions, respectively, and pH detection of the equivalence point. Total sulfate concentration was determined by titration with barium chloride using conductimetric measurements to detect the equivalence point.

3.1. Experimental studies of ions and water transport on a laboratory scale

Experiments were carried out in a laboratory two-compartment plate-and-frame cell equipped with an oxygen evolving DSA[®] as anode, a nickel cathode and using Nafion[®] 350 membrane. Electrodes and membrane active area was 75 mm high and 42 mm wide. Each compartment was 12 mm wide. The electrolytes were recycled repeatedly through the cell and through thermostated 250 ml or 2 l reservoirs. The 2 l reservoir was used in the anolyte or catholyte circuit in order to operate under constant conditions because of the large volume. The 250 ml reservoir, a graduated cylinder, was used in the remaining circuit to enable the measurements (concentrations and volume variations). A sodium sulfate and sulfuric acid mixture and a sodium hydroxide solution were fed, respectively, to the anolyte and catholyte compartments. Temperature was controlled at $50 \pm 1^\circ\text{C}$. Pressure control was done to minimise the pressure driven transmembrane water flux. Constant current was supplied by a d.c. power supply. The electrolyte volume variations were measured after the current was turned off and all gas bubbles were disengaged.

The effects of the following parameters on sodium transport number and water flux through the membrane were studied in the ranges given: (i) current density

(1000–7000 A m⁻²); (ii) sulfuric acid to total sulfate concentration ratio (0–0.7); (iii) sodium hydroxide concentration (4–5.4 mol dm⁻³); (iv) electrolyte flow velocities (0.03–0.1 m s⁻¹); and (v) total sulfate concentration (2–2.5 mol dm⁻³).

3.2. Experimental study of a feed and bleed process in pilot scale

Electrolysis was investigated using a pilot plant with the ElectroSynCell electrolyser supplied by Electrocell AB. The electrodes and the membrane used were the same as those used in the laboratory cell. The active area was 0.04 m² (28.3 cm high and 14.1 cm large). Each compartment was 3 mm wide (i.e., the width of the turbulent promoter placed between the membrane and the electrode). Electrolyte flow velocities were varied from 4 to 40 cm s⁻¹. A feed and bleed operation was performed. The inlet flows were mixed with the recycled streams in two 30 l reservoirs. Flowrates are adjusted so as to equalise the pressures in the compartments.

The effect of sulfuric acid to total sulfate concentration ratio was studied, as it is the main parameter (see below). Electrolyte temperature was maintained at 50 ± 2 °C and the current density at 3000 A m⁻². Other operating conditions are reported in Table 1.

4. Results and discussion

4.1. Membrane properties study in a laboratory scale

4.1.1. Sodium transport

The sodium transport number t_{m,Na^+} is determined as the ratio of sodium flux through the membrane during time $\Delta\theta$ to the number of moles of charge passing in the cell during the same time:

$$t_{m,Na^+} = \frac{(V_c[Na^+]_c)_{\theta+\Delta\theta} - (V_c[Na^+]_c)_\theta}{Js\Delta\theta/F} = \frac{(V_a[Na^+]_a)_\theta - (V_a[Na^+]_a)_{\theta+\Delta\theta}}{Js\Delta\theta/F} \quad (8)$$

Extensive studies show that current density, total sulfate concentration and electrolytes flow velocities have no effect on the transport of sodium through the membrane. The same is observed concerning sodium hydroxide concentration within the range of investigation, that is, 4–5.4 mol dm⁻³ (for low acid concentration, say about 0.05 mol dm⁻³, sodium transport number varies from 0.89 to 0.85 with a tendency to decrease when sodium hydroxide concentration increases). The main factor is the sulfuric acid to total sulfate concentration ratio. Hereafter, this ratio will be denoted X . (i.e., $X = C_H/2C_{SO_4}$).

Under our conditions, when X is greater than 0.25, this parameter determines sodium transport. When X is low ($X < 0.2$), it seems that this factor is no longer important and the sodium transport number is nearly constant. Figure 3 represents the variations of sodium ion transport number through the membrane against X . Two zones are clearly identified: zone II where ion transport is controlled by anolyte composition because the membrane is in ‘acidic state’; and, conversely, zone I when the membrane is in ‘alkaline state’ and the transport is controlled by the catholyte. The leakage of hydroxyl ion explains why the current efficiency value is not 100% when no acid is present. The hydroxyl ion leakage depends on the sodium hydroxide concentration. These results are in accordance with Jørisen et al. [2].

For $0.25 < X < 0.7$, the value of t_{m,Na^+} may be obtained by the following equation (the interval given for each parameter corresponds to a 95% confidence):

$$t_{m,Na^+} = (1.16 \pm 0.04) - (1.36 \pm 0.09)X \quad (9)$$

Table 1. ElectroSynCell steady-state feed and bleed operation

| | Inlet conditions | Experimental outlet values | Calculated values | Discrepancy (%) |
|--|---|---|--------------------------------------|-----------------|
| (a) | | | | |
| [H ₂ SO ₄] = C _H /2 | 0 | 0.66 mol dm ⁻³ | 0.66 mol dm ⁻³ | <1 |
| C _{SO₄} = [H ₂ SO ₄] + [Na ₂ SO ₄] | 2.11 mol dm ⁻³ | 2.28 mol dm ⁻³ | 2.32 mol dm ⁻³ | <2 |
| NaOH | 2.93 mol dm ⁻³ | 3.94 mol dm ⁻³ | 3.82 mol dm ⁻³ | 3.1 |
| Anolyte flowrate | 2.9 ± 0.05 dm ³ h ⁻¹ | 2.7 ± 0.05 dm ³ h ⁻¹ | 2.64 dm ³ h ⁻¹ | 2.3 |
| Catholyte flowrate | 3.0 ± 0.05 dm ³ h ⁻¹ | 3.2 ± 0.05 dm ³ h ⁻¹ | 3.21 dm ³ h ⁻¹ | <1 |
| (b) | | | | |
| [H ₂ SO ₄] = C _H /2 | 0.42 | 0.97 mol dm ⁻³ | 0.96 mol dm ⁻³ | 1 |
| C _{SO₄} = [H ₂ SO ₄] + [Na ₂ SO ₄] | 2.15 mol dm ⁻³ | 2.35 mol dm ⁻³ | 2.36 mol dm ⁻³ | 1 |
| NaOH | 3.06 mol dm ⁻³ | 3.70 mol dm ⁻³ | 3.68 mol dm ⁻³ | <1 |
| Anolyte flowrate | 3.0 ± 0.05 dm ³ h ⁻¹ | 2.78 ± 0.05 dm ³ h ⁻¹ | 2.73 dm ³ h ⁻¹ | <2 |
| Catholyte flowrate | 3.1 ± 0.05 dm ³ h ⁻¹ | 3.32 ± 0.05 dm ³ h ⁻¹ | 3.32 dm ³ h ⁻¹ | <1 |
| (c) | | | | |
| [H ₂ SO ₄] = C _H /2 | 0.80 | 1.24 mol dm ⁻³ | 1.22 mol dm ⁻³ | <2 |
| C _{SO₄} = [H ₂ SO ₄] + [Na ₂ SO ₄] | 2.12 mol dm ⁻³ | 2.35 mol dm ⁻³ | 2.32 mol dm ⁻³ | 1.3 |
| NaOH | 3.01 mol dm ⁻³ | 3.43 mol dm ⁻³ | 3.41 mol dm ⁻³ | <1 |
| Anolyte flowrate | 3.15 ± 0.05 dm ³ h ⁻¹ | 2.86 ± 0.05 dm ³ h ⁻¹ | 2.88 dm ³ h ⁻¹ | <1 |
| Catholyte flowrate | 3.15 ± 0.05 dm ³ h ⁻¹ | 3.39 ± 0.05 dm ³ h ⁻¹ | 3.37 dm ³ h ⁻¹ | <1 |

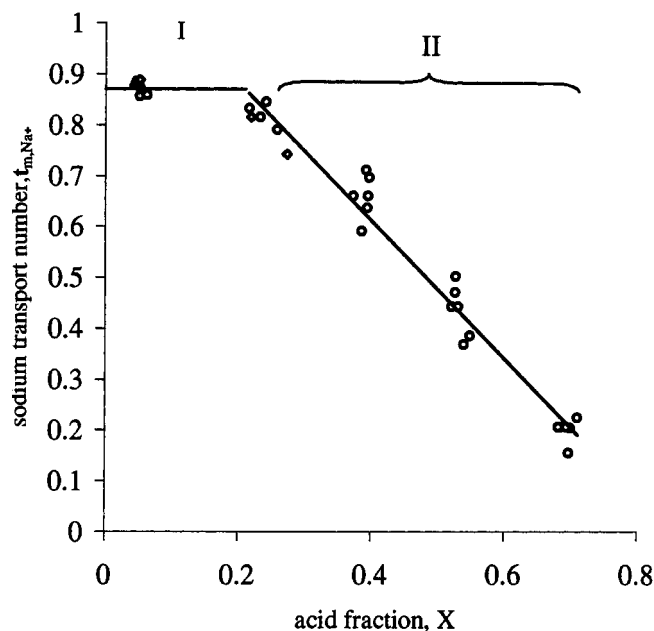


Fig. 3. Sodium transport number against sulfuric acid to total sulfate concentration ratio X . Different sets of operating parameters: current density, total sulfate, flow velocity, sodium hydroxide 4–5 M.

For $X < 0.2$, the value of t_{m,Na^+} is nearly constant in the sodium hydroxide concentration range (4–5.4 mol dm⁻³):

$$t_{m,Na^+} = 0.87 \pm 0.02 \quad (10)$$

4.1.2. Membrane selectivity

To determine the membrane preferential permselectivity to sodium ion relative to hydrogen ion, the hydrogen ion concentration must be determined in H₂SO₄–Na₂SO₄ mixture. Owing to the high and variable ionic strength (up to 6 mol dm⁻³) it is not possible to determine the required concentration precisely either experimentally or by thermodynamic calculations. As an approximation, we use the results of the studies of Pitzer et al. [9, 10]. The dissociation constant of HSO₄⁻ is given as a function of the temperature. The interaction parameters are also given (some parameters are not known and the authors suggest to use those of other similar electrolytes). The equations used were tested by comparing calculated and experimental dissociation of sulfuric acid at 25°C. H⁺ concentration may be determined as a function of X and C_{SO_4} . The permselective coefficient of sodium ion relative to hydrogen ion is defined as follows:

$$P_{H^+}^{Na^+} = \frac{t_{m,Na^+}[H^+]}{t_{m,H^+}[Na^+]} \quad (11)$$

Figure 4 represents the variation of this coefficient against X . The permselective coefficient is nearly constant except at low acid concentrations where the membrane is in ‘alkaline state’. The membrane affinity

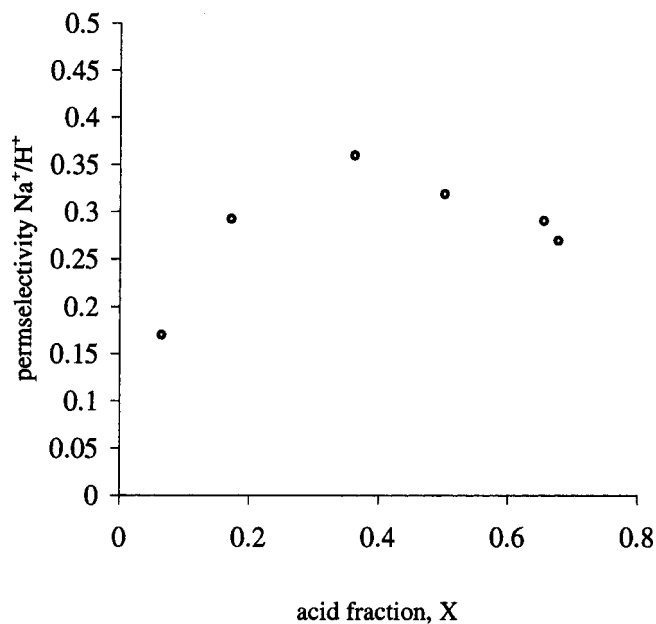


Fig. 4. Permselective coefficient of Na⁺ relative to H⁺ against sulfuric acid to total sulfate ratio.

for H⁺ is about three times higher than for sodium ion. This is in accordance with the known values of Na⁺ and H⁺ diffusion coefficient in Nafion[®] 117 membrane (0.98×10^{-6} and 3.5×10^{-6} cm² s⁻¹, respectively) [11]. It is assumed that these values are still valid in Nafion[®] 350 membrane.

4.1.3. Water transport

Careful measurements of anolyte volume variations are undertaken. Figure 5 reports these results as volume

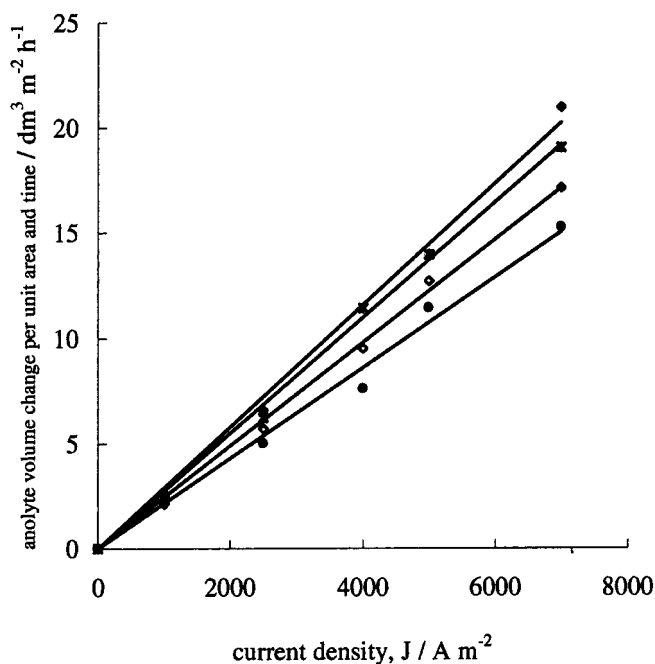


Fig. 5. Anolyte volume change per membrane area and time against current density. Concentration ratio, X : (◆) 0.05, (×) 0.23, (◇) 0.52 and (●) 0.69 (top to bottom).

change per unit area and unit time against the current density and for different X values. The volume variations are mainly a function of the charge passing in the system. The factor X has a limited influence on water balance and other parameters such as sodium hydroxide concentration and flow velocity have no effect. The following relation is obtained:

$$-\Delta V_a = \alpha \frac{Js\Delta\theta}{F} = \alpha n_{th} \quad (12)$$

where n_{th} denotes the molar charge (in faraday) passing in the cell during time $\Delta\theta$. Figure 6 represents the effect of X on the value of α . The following relation gives a good approximation for α in $\text{dm}^3 \text{ faraday}^{-1}$:

$$\alpha = 0.078 - 0.029X \quad (13)$$

To obtain water transport through the membrane, the mass balance of the anode compartment is written:

$$-d(\rho_a V_a) = dm_m + (t_{m,Na^+}M_{Na^+} + (1 - t_{m,Na^+})M_{H^+}) \times \frac{Js d\theta}{F} + \frac{M_{O_2}}{4} \frac{Js d\theta}{F} \quad (14)$$

The different terms are, respectively, mass variation in the anolyte, mass of water transported through the membrane, mass of sodium and hydrogen ions that migrate through the membrane and mass of oxygen produced at the anode during time $d\theta$.

If the anolyte density is assumed nearly constant, Equations 12 and 14 enable the calculation of the specific flowrate of water through the membrane:

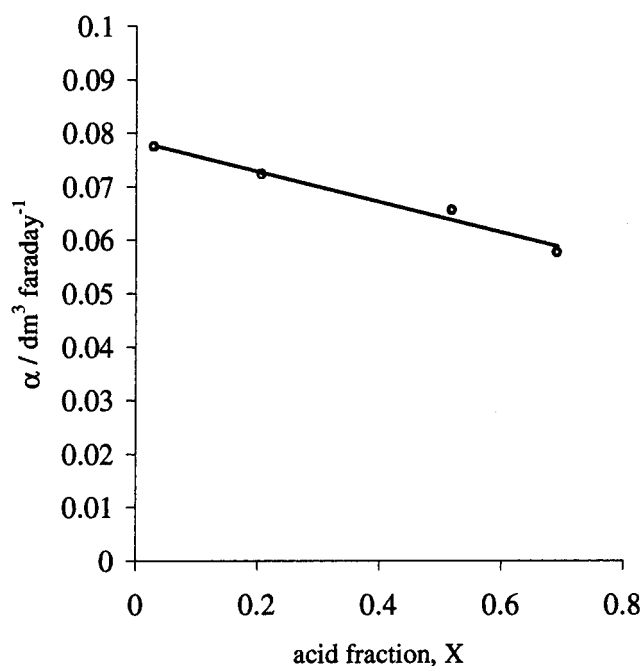


Fig. 6. α against sulfuric acid to total sulfate concentration ratio.

$$W = \frac{dm_m}{sd\theta} = \frac{m_m}{s} = \frac{J}{F} \left(\alpha \rho_a - (t_{m,Na^+}M_{Na^+} + (1 - t_{m,Na^+})M_{H^+}) - \frac{M_{O_2}}{4} \right) \quad (15)$$

The term $(1 - t_{m,Na^+})M_{H^+}$ in Equations 14 and 15 must be replaced by $-(1 - t_{m,Na^+})M_{OH^-}$ in the membrane alkaline state.

Specific flowrate variations as a linear function of current density suggest an electroosmosis mechanism for water transport. The water transport number is defined as the number of water molecules transferred when one faraday passes in the system, that is,

$$t_{m,H_2O} = \frac{FW/M_{H_2O}}{J} \quad (16)$$

When the membrane is in acidic state, t_{m,H_2O} represents the number of water molecules connected to the transport of one mole of cations through the membrane (Na^+ and H^+). Due to the hydrophobic nature of the perfluorinated membrane, water transport concerns mainly water of the ion hydration sphere [12]. Water transport number (as defined by Relation 16) is reported in Figure 7 curve (a) against X (for $X < 0.2$ the curve is in dotted line).

In the 'acidic state' of the membrane, water transport number represents the average number of water molecules transported by sodium and hydrogen ions (part of curve (a) in full line).

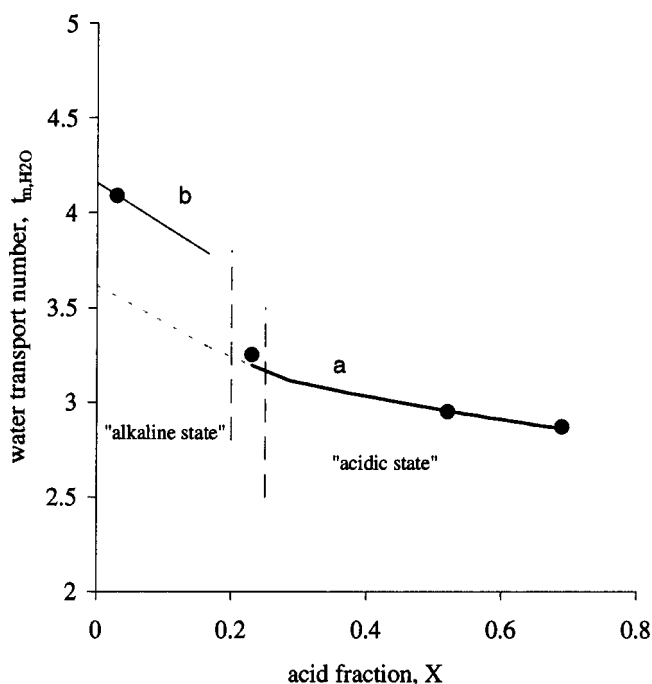


Fig. 7. Curve (a): Water transport number against sulfuric acid to sulfate concentration ratio. Curve (b): Water to sodium molar ratio during transfer through the membrane in the 'alkaline state'.

In the 'alkaline state' of the membrane, OH^- and Na^+ are the current carriers. W is the amount of water crossing the membrane from anolyte to catholyte. Consequently, only sodium ions are responsible of this transfer. The curve marked (b) in the 'alkaline region' represents the ratio of water molecules to sodium flux through the membrane. The intermediate case is not considered.

It appears that sodium ion migrates through the membrane with about four moles of water per mole of ion. Hydrogen ions take about three (or less) water moles per mole of ion. These values are consistent with other results [12, 13].

4.2. Pilot scale tests

4.2.1. Predictions of a steady-state feed and bleed operation

To predict the electrolysis results in steady-state feed and bleed operation Equations 1 or 2, 3 to 7, 9 or 10, 13 and 15 must be solved. In addition, densities of the electrolytes must be known. Anolyte density is a function of X and C_{SO_4} and catholyte density is a function of sodium hydroxide concentration (see Appendix 1). The numerical computation enables the determination of the variables $Q_{\text{out},a}$, $Q_{\text{out},c}$, $C_{\text{Hout},a}$, $[\text{Na}^+]_{\text{out},a}$, total sulfate in the anolyte outlet, sodium transport number (i.e., current efficiency), $[\text{OH}^-]_{\text{out},c}$ etc. The calculation flow-chart is given in Figure 12 of Appendix 2.

4.2.2. Experimental validation tests

Figures 8 and 9 give examples of experimental acid and alkali concentrations versus time and show the steady-state attainment. During these experiments, the start-up

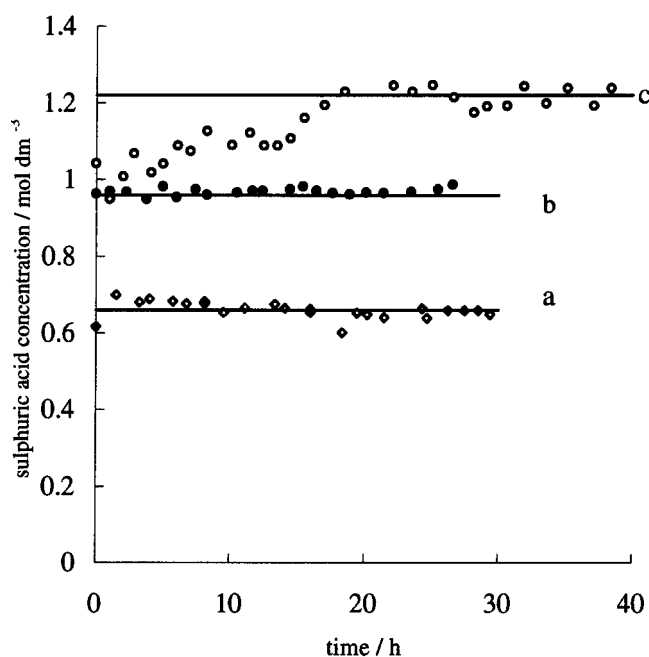


Fig. 8. Sulfuric acid concentration in the outlet stream against elapsed time during feed and bleed operation. (a), (b) and (c) refer to conditions given in Tables 1(a), (b) and (c), respectively.

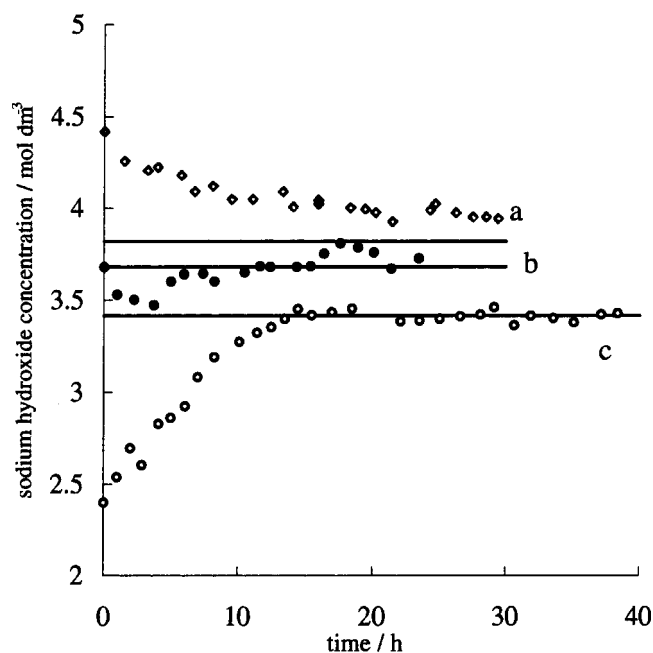


Fig. 9. Sodium hydroxide concentration in the outlet stream against elapsed time during feed and bleed operation. (a), (b) and (c) refer to conditions given in Tables 1(a), (b) and (c), respectively.

conditions are taken near the predicted values, which are represented by continuous lines in the figures.

Table 1 report experimental results compared to the predicted values. In the steady-state, sodium mass-balance is checked within 1.5%. In case (a) it seems that steady-state is not really reached in the soda compartment. Moreover, the discrepancy is never higher than 3.1%. The good agreement of experimental values with the predictions confirms the validity of the model and the pertinence of the use of the laboratory results for a pilot plant with a scaling factor of about 13.

4.2.3. Cascade electrolysis

The decrease in current efficiency when the acid to salt ratio increases (i.e., when the salt conversion rate increases) suggests the use of a cascade of electrolyzers working in series as shown in Figure 10. Only the last cell operates at the high final concentration of sulfuric acid with the subsequent low current efficiency. The early stages operate at lower acid concentration and have higher current efficiencies. Thus, the resulting average current efficiency increases when the number of stages increases. Each cell may be designed by solving the equations given above and by using the outlet values for the preceding cell as input values. The area of each cell may be obtained when the salt conversion is known.

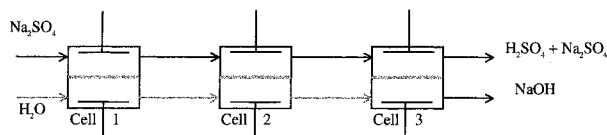


Fig. 10. Cascade of three cells in series.

Moreover, the cascade may be optimized but this is not done in this work.

Let us compare a cascade of three stages in series (a reasonable number) and a single stage for sulfuric acid and soda production. All the stages include two-compartment cells processing in feed and bleed mode (as shown in Figure 2). It is assumed that a steady-state is reached. Sodium sulfate concentration in the feed is 2 mol dm^{-3} and no acid is present. Soda inlet concentration is taken as 3 mol dm^{-3} . The final conversion ratio to achieve is fixed to 0.6. It is assumed, arbitrarily, that the cascade operates at $X = 0.33, 0.5$ and 0.6 for the three cells, respectively. Table 2 reports the results. Some parameters like C_{SO_4} vary out of the range of our experimental investigation. We assume the validity of the relations giving sodium transport number and density. From Table 2, it appears that the area needed to split the same quantity of salt is, as expected, lower in the case of the cascade and current efficiency is better than in the case of a single stage. The example is not optimized but it shows a reduction of membrane and electrodes area of about 33% and an increase of current efficiency from 34% to 54%. Also the alkali concentration is higher and the transport of water through the membrane is reduced. It is obviously an advantage to use cascaded cells.

Table 2. Comparison of a single stage ($X = 0.6$) and three-stages in series ($X_1 = 0.33, X_2 = 0.5$ and $X_3 = 0.6$). Current density = 3000 A m^{-2}

| | Single stage | 3 stages in series |
|--|------------------------------------|------------------------------------|
| Anolyte outlet flowrate | $545 \text{ dm}^3 \text{ h}^{-1}$ | $732 \text{ dm}^3 \text{ h}^{-1}$ |
| [H ₂ SO ₄] stage 1 | 2.20 mol dm^{-3} | 0.75 mol dm^{-3} |
| stage 2 | | 1.24 mol dm^{-3} |
| stage 3 | | 1.64 mol dm^{-3} |
| [Na ₂ SO ₄] stage 1 | 1.47 mol dm^{-3} | 1.50 mol dm^{-3} |
| stage 2 | | 1.24 mol dm^{-3} |
| stage 3 | | 1.09 mol dm^{-3} |
| Sodium hydroxide outlet flowrate | $1384 \text{ dm}^3 \text{ h}^{-1}$ | $1217 \text{ dm}^3 \text{ h}^{-1}$ |
| [NaOH] stage 1 | 3.90 mol dm^{-3} | 3.98 mol dm^{-3} |
| stage 2 | | 4.32 mol dm^{-3} |
| stage 3 | | 4.44 mol dm^{-3} |
| Electroosmosis | | |
| stage 1 | $414 \text{ dm}^3 \text{ h}^{-1}$ | $106 \text{ dm}^3 \text{ h}^{-1}$ |
| stage 2 | | $77 \text{ dm}^3 \text{ h}^{-1}$ |
| stage 3 | | $64 \text{ dm}^3 \text{ h}^{-1}$ |
| total | $414 \text{ dm}^3 \text{ h}^{-1}$ | $247 \text{ dm}^3 \text{ h}^{-1}$ |
| Current efficiency | | |
| stage 1 | 0.34 | 0.71 |
| stage 2 | | 0.48 |
| stage 3 | | 0.34 |
| global | 0.34 | 0.54 |
| Active area | | |
| stage 1 | 62.3 m^2 | 16.9 m^2 |
| stage 2 | | 12.4 m^2 |
| stage 3 | | 10.4 m^2 |
| total | 62.3 m^2 | 39.7 m^2 |

Inlet conditions: sodium sulfate flowrate = $1000 \text{ dm}^3 \text{ h}^{-1}$, concentration = 2 mol dm^{-3} ; sodium hydroxide flowrate = $1000 \text{ dm}^3 \text{ h}^{-1}$, concentration = 3 mol dm^{-3} .

5. Conclusion

Sodium sulfate electrochemical splitting in a two-compartment cell with a cation exchange membrane produces sulfuric acid and, therefore, free hydrogen ion. The high mobility of hydrogen ion compared to sodium ion (the permselective coefficient of hydrogen ion relative to sodium ion in Nafion® 350 membrane is about 3) is unfavourable for the process. As salt conversion increases, current efficiency decreases.

Sodium transport number and water flow through the membrane are determined in a laboratory cell equipped with Nafion® 350 membrane. The membrane is either in 'acidic state' or in 'alkaline state' depending on whether hydrogen ions or hydroxyl ions cross the membrane. Anolyte sulfuric acid to total sulfate concentration ratio (respectively catholyte concentration) controls ions transport in the 'acidic state' (respectively in the 'alkaline state'). Water is transferred through the membrane by an electroosmosis mechanism. The experimental values of water transport number are close to hydration numbers of sodium and hydrogen ions due to the hydrophobic nature of the Nafion® 350 membrane.

The knowledge of sodium and water transport numbers and the mass-balance applied to a continuous feed and bleed operation at the steady-state enable the predictions of the process. Tests were performed in a pilot plant, where the active area is 13 times higher than the laboratory case. Experimental outlet flowrates and concentrations follow closely the predictions. Although the laboratory and the pilot cells are not geometrically similar (compartment width and turbulent promoter differ) the membrane behaviour is not changed because it is related to either the anolyte or the catholyte composition. Thus, the model given is suitable to calculate a large-scale process and may be used for industrial purposes. As a consequence of the decrease of current efficiency when salt conversion increases (in practical cases the membrane will be in the 'acidic state') it will be advantageous to use a cascade of cells in series.

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Appendix 1: Densities of sodium hydroxide solutions and of sodium sulfate–sulfuric acid mixtures at 50 °C

Sodium hydroxide

Sodium hydroxide solution density is a function of concentration. The values are reported in [14]. At 50 °C, the following relation fits the data:

$$\rho_c = -0.00076 [\text{NaOH}]^2 + 0.04028 [\text{NaOH}] + 0.98807 \quad (17)$$

Sodium sulfate–sulfuric acid mixtures

Densities were determined by a standard method using a picnometer. Table 3 gives the values at $50 \pm 0.2^\circ\text{C}$.

Solution density ρ_a varies linearly with C_{SO_4} . Zero-intercept of each line ρ_a against C_{SO_4} is fixed at the value of water density at 50°C ($=0.98807$). The slope depends on the ratio of acid to total sulfate. The following relation is consistent with the data:

$$\rho_a = (0.0175X^2 - 0.069X + 0.1108)C_{\text{SO}_4} + 0.98807 \quad (18)$$

Figure 11 reports experimental values compared to those given by Relation 18. The correlation is high.

Table 3. Density of H_2SO_4 – Na_2SO_4 mixtures (in kg dm^{-3}) at 50°C (C_{SO_4} is total sulfate concentration and X is sulfuric acid to total sulfate concentration ratio)

| X | $C_{\text{SO}_4}/\text{mol dm}^{-3}$ | | | |
|-----|--------------------------------------|--------|--------|--------|
| | 2.6 | 2.4 | 2.2 | 2.0 |
| 1.0 | 1.1406 | 1.1290 | 1.1173 | 1.1056 |
| 0.8 | 1.1606 | 1.1474 | 1.1352 | 1.1219 |
| 0.6 | 1.1822 | 1.1686 | 1.1531 | 1.1396 |
| 0.4 | 1.2090 | 1.1935 | 1.1762 | 1.1611 |
| 0.2 | 1.2409 | 1.2222 | 1.2049 | 1.1862 |
| 0.0 | 1.2729 | 1.2529 | 1.2326 | 1.2121 |

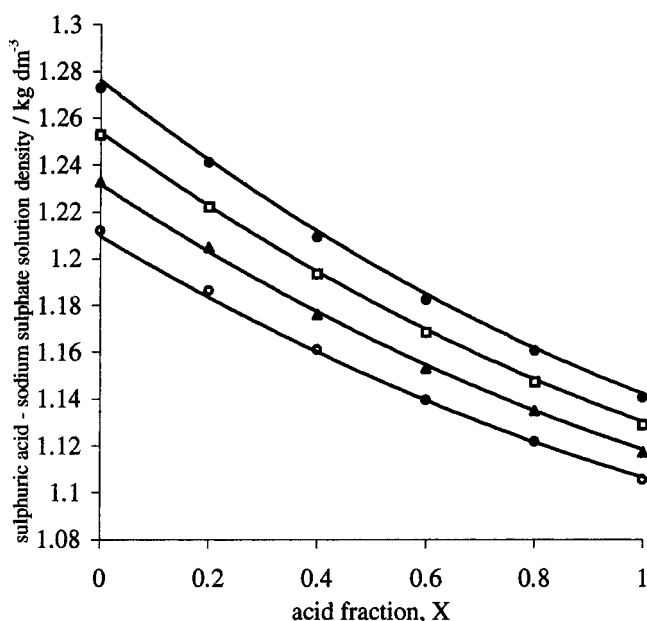


Fig. 11. Densities of mixtures of H_2SO_4 and Na_2SO_4 against sulfuric acid to total sulfate concentration ratio for different values of C_{SO_4} . Curves are given by Equation 14. From bottom upwards, $C_{\text{SO}_4} = 2; 2.2; 2.4; 2.6 \text{ M}$.

Appendix 2: Numerical computation for cell design

The procedure to solve mass-balance equations describing a steady-state feed and bleed operation is given in Figure 12. The variables to enter are the inlet flows concentrations and flowrates, current density and the active area of the cell. A trial and error method enables the determination of current efficiency (i.e., sodium

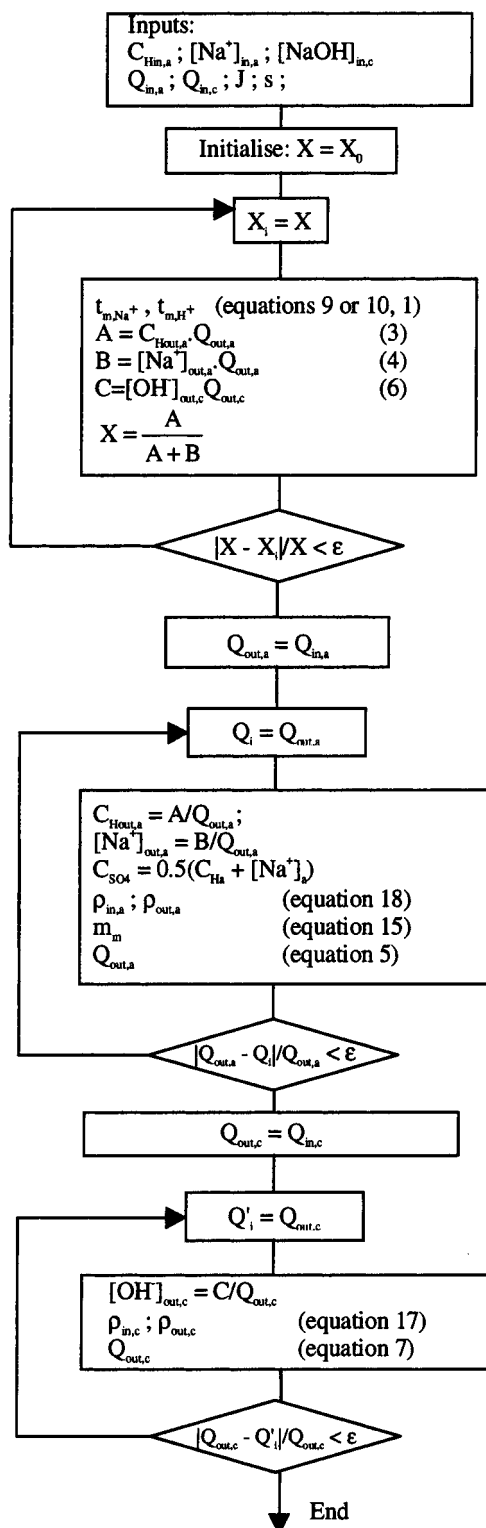


Fig. 12. Numerical computation for cell design.

transport number) and sulfuric acid to total sulfate concentration ratio. The other variables are determined by two successive trial and error calculations.

The same procedure is followed for cell design (determination of the necessary electrodes and membrane area to achieve a given salt conversion).

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